



PCT/AU00/01001

10/070218

REC'D 11 SEP 2000

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I, KAY WARD, TEAM LEADER EXAMINATION SUPPORT AND SALES
hereby certify that annexed is a true copy of the Provisional specification in
connection with Application No. PQ 2465 for a patent by JAMES HARDIE
RESEARCH PTY LIMITED filed on 26 August 1999.

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AUSTRALIA

PATENTS ACT 1990

PROVISIONAL SPECIFICATION

FOR THE INVENTION ENTITLED:-

"EXTRUDABLE CEMENTITIOUS MATERIAL "

The invention is described in the following statement:-

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TECHNICAL FIELD

The present invention relates to building products and particularly fibre reinforced cement building products.

BACKGROUND ART

5 Fibre reinforced cement boards and other products have been widely used as materials for walls, ceilings, roofs, floors etc: of buildings and for substitutes for wood trim, frames etc.

There are many methods for forming and shaping such FRC products including Hatschek sheet process. Mazza pipe process, Magnani sheet process, injection
10 moulding, hand lay-up, casting, filter pressing, roll forming etc.

Extrusion of fibre cement products has been performed on a limited basis but it has a number of difficulties which have reduced its commercial viability. In the extrusion process, the cementitious slurry or paste is forced through a die and the material can be subjected to elevated pressures. For this reason, it is important that the slurry or paste
15 has good flow characteristics. The cementitious formulation often contains elements that are present almost entirely as process aids, increasing the flow properties, the shape retention properties or enhancing the surface finish. A common type of these additives can be broadly classified as viscosity enhancing agents (VEA) or 'binders'. A principal function on these is to increase the viscosity of the liquid phase, and to counter problems
20 such as segregation of the liquid and solid phases ('water retention'), lack of shape retention, non uniform dispersion of the solid components etc.

For materials such as clays extruded in the brick and tile industry, the inherent good flow properties of the clay mean that the use of such VEA's may be minimised, and therefore cheap. However when the solids suspensions that require forming are not
25 plastic (such as cementitious slurries or pastes), and inherently resistant to flow, the additives are often expensive high molecular weight organic polymers. Further, the demand for viscosity enhancing agents can be increased by the presence of reinforcing fibres, specially if these are hard to disperse or do not have good water retention characteristics.

30 Asbestos generally has better dispersion and water retention properties than pulp fibres, and when used as reinforcement in cementitious compositions, require less

extensive use of viscosity enhancing agents, however, as is well-known in the art, the use of asbestos fibres is outlawed in many countries and is undesirable even in those countries where its use is legal.

Accordingly, previous efforts in finding reinforcing fibres for extrudable cementitious pastes have concentrated on non-asbestos fibres and, in particular, choosing or treating such non-asbestos fibres so that their dispersion and water retention characteristics make them suitable for use in extrusion moulding with minimal use of viscosity enhancing agents. For instance, US patent no 5,891,374 discloses a process for producing a fibre reinforced cement matrix composite. In this document, hydraulic cement, water and low quantities of water soluble binder are mixed together with synthetic fibres to produce an extruded and cured composite product. Optionally, a water reducing agent may be added to assist in preferential alignment of the fibres in the load bearing direction.

Such synthetic fibres are commonly used. However, they are expensive and some are unable to be cured at high temperatures such as in an autoclave. Currently, wood pulp fibres remain a fibre of choice for reinforcing cement composites for building materials, where they show excellent performance with regard to mechanical strength, toughness and durability at a low cost. However, extrudable cement compositions containing wood pulp fibres have very stringent requirements for rheology modification and require expensive high molecular weight organic polymers as viscosity enhancing agents.

It is believed that the viscosity enhancing agent performs two functions. Firstly, it acts as a high solid suspension thickener to increase the water retention properties of the slurry, and secondly, it also lubricates the suspended particles thereby allowing the high solid suspension to flow under deformation without phase separation and segregation.

The effectiveness of such a viscosity enhancing agent is believed to be a combination of three actions, namely:

adsorption of water by long-chain polymer molecules, increasing viscosity of the mixed water,

association of adjacent polymer chains, further blocking the motion of water, and

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intertwining and entangling of the polymer chains, thereby behaving in a sheer thinning manner.

For suspensions involving cement and pulp fibre that are processed by extrusion, the commonly used viscosity enhancing agents are high viscosity cellulose ethers such as methyl cellulose, hydroxypropyl methyl cellulose or hydroxyethyl methyl cellulose. US Patent 5,047,086 discloses the use of extremely high viscosity ($>80,000$ cps @ 2% solution at 20°C) alkylcellulose and/or hydroxyalkylalkylcellulose at 0.2-1 wt % levels in the preparation of these compositions. This patent also discloses that if lower viscosity ($12,000$ - $40,000$ cps @ 2% solution at 20°C) grades of these compounds (akin to those used in asbestos fibre/cement extrusion compositions) are used, much higher addition levels are required.

Even when these mouldings are made with the minimisation of the use of viscosity enhancing agents by using the high viscosity grades, the cost ratio of required viscosity enhancing agents to the total cost of the extruded moulding can be in the order of one fourth to one half. Thus it is clear that any method of reducing the amount of viscosity enhancing agents required to attain excellent mouldability, is greatly to be desired.

Furthermore, highly effective viscosity enhancing agents like hydroxypropyl methylcellulose (HPMC) and hydroxyethyl methylcellulose (HEMC) experience a phenomenon known as high temperature gelation. That is, the viscosity of the viscosity enhancing agents undergoes a sharp increase when the temperature exceeds a specific limiting temperature, known as the gel temperature. The gel temperature of these viscosity enhancing agents varies with the exact chemistry (i.e. degree of substitution etc.). Though this phenomenon can be useful in some applications, it is limiting in others. For example, cooling jackets are sometimes required to counter the temperature rise in the extruder barrel during long periods of fast running, to keep the extrudate below the gel temperature of the viscosity enhancing agent being used. Viscosity enhancing agents with higher gel temperatures are sought after in these circumstances to avoid this complication. Hence, the ability to use a type of viscosity enhancing agent that does not undergo thermal gelation (like hydroxyethyl cellulose (HEC)) would be a great advantage in certain applications.

The present invention seeks to ameliorate at least some of the disadvantages of the prior art or provide a commercial alternative thereto.

DISCLOSURE OF THE INVENTION

5 In a first aspect, the present invention provides an agent for treating a cementitious slurry, comprising a viscosity enhancing agent and a dispersion agent in a quantity sufficient to increase the efficacy of the viscosity enhancing agent.

In another aspect, the invention provides an extrudable cementitious dough or paste formed by mixing 0.3-5 % by weight of dry solids of viscosity enhancing agent and 0.05-0.5 % by weight of dry solids of dispersion agent to water and a cementitious
10 material, optionally with lime, silica, density modifiers, reinforcing fibres etc and water.

The applicant has found that by the addition of a suitable dispersion agent, the efficacy of the viscosity enhancing agent can be improved. The reference to the efficacy of the viscosity enhancing agent being improved refers to the fact that the addition of a suitable dispersion agent allows a lower grade (and cheaper) viscosity enhancing agent
15 to be used or alternatively if a higher grade is used, less viscosity enhancing agent is required.

Dispersion agents, also known as plasticisers or super plasticisers, have long been used in the concrete industry to improve paste workability or to increase fluidity. The attraction forces existing amongst the cement particles that cause agglomeration are
20 neutralised by adsorption of anionic polymers. The dispersion of these cement particles is related to the electrical repulsion produced by the absorption of the negatively charged group. This mechanism has been confirmed in sulfonated-type dispersion agents such as sulfonated melamine formaldehyde and sulfonated naphthene formaldehyde. The dispersion mechanism for acrylic polymers is believed to be ascribed to a steric
25 hindrance effect rather than electrostatic repulsion. These dispersion agents, however, have not been used as rheology modifiers in fibre reinforced cement slurry.

The applicant has found a surprising synergy between viscosity enhancing agents and dispersion agents. The combination of viscosity enhancing agent and dispersion agent is far superior in terms of rheology modification than either component alone. The
30 addition of the dispersion agent allows use of a far broader range of viscosity enhancing agents than have otherwise been proposed. To explain, as mentioned above, the most

common viscosity enhancing agents are hydroxypropylmethyl cellulose, hydroxyethylmethyl cellulose and methyl cellulose. These products are quite expensive and accordingly large additions are preferably avoided.

By combining the viscosity enhancing agent with a dispersion agent, the effectiveness of the viscosity enhancing agent is increased, thereby reducing the quantity required. Further, cheaper viscosity enhancing agents can be used such as lower grade hydroxypropylmethyl cellulose or hydroxyethyl cellulose. These cheaper viscosity enhancing agents can be around half the cost of high grade cellulose ethers.

Examples of high grade viscosity enhancing agents are high molecular weight cellulose ethers, for example alkylcellulose or hydroxyalkyl alkylcellulose. Low grade VEA's can be the same compounds at a lower molecular weight. Suitable viscosity enhancing agents for use with the present invention include methyl cellulose, hydroxyethyl cellulose, hydroxyethylmethyl cellulose, hydroxypropylmethyl cellulose, carboxymethyl cellulose, ethyl cellulose, hydroxybutylmethyl cellulose, polyvinyl alcohol, clays, modified clays, Welan gum and other natural gums. The viscosity enhancing agent and/or dispersion agent can be added together or separately to the cementitious slurry or indeed included in the dry formulation prior to slurry preparation. As will be clear to persons skilled in the art, it is important that the dispersion agent and viscosity enhancing agent are thoroughly mixed through the slurry to provide a homogeneous mix.

The current invention enables the forming of compositions with excellent mouldability and workability and yet enables the reduction of cost due to viscosity enhancing agents, by both allowing the use of less viscosity enhancing agents and allowing the use of lower (cheaper) grades of viscosity enhancing agents. The addition of 0.05-0.5 wt. % of a dispersion agent, can result in the requirement for viscosity enhancing agents falling by ~20% and/or a less potent viscosity enhancing agent being used with equivalent or better extrusion mouldability than compositions with the conventional levels of viscosity enhancing agent.

Suitable dispersion agents include sulfonated melamine formaldehyde, sulfonated naphthalene formaldehyde, amino-sulfonate polymer, modified lignosulfonate materials

and acrylic polymers such as copolymer of acrylic acid with acrylic ester, copolymers of acrylic acid with polycarboxylate ester and cross-linked acrylic polymers.

Accordingly, in another aspect, the present invention provides a method of treating a cementitious material to improve its extrudability, said method comprising adding to
5 the cementitious material in combination, 0.3-5 % by weight of dry solids of viscosity enhancing agent and 0.05-0.5 % by weight of dry solids of dispersion agent is added.

As discussed above, it is important when extruding a cementitious paste or slurry that stringent rheological criteria are met while minimising the cost due to the use of viscosity enhancing agents.

10 In order to determine suitable quantities of viscosity enhancing agent and dispersion agent, a simple extrusion test may be conducted whereby a cementitious paste is provided including the viscosity enhancing agent and dispersion agent and applied to a test die at a test pressure to confirm extrudability. As it will be clear to persons skilled in the art, exact quantities of viscosity enhancing agent and dispersion agent will depend on
15 a number of factors including the type of agent used, the content of the cementitious paste and indeed the extrusion equipment in which the cementitious paste will be used.

The extrudable cementitious material may also be provided as a dry formulation, with water to provide a cementitious paste or slurry, being added shortly before extrusion. The viscosity enhancing agent and dispersion agent can be added
20 simultaneously or separately to the composition. The viscosity enhancing agent and dispersion agent can be added as dry solids, either before or after the addition of water to the other solid components. The viscosity enhancing agent and dispersion agent can also be dispersed in water first and then added to the other solid component. Liquid, solid, solution, emulsion or suspension forms of viscosity enhancing agents and dispersion
25 agents can be used.

In other words, it is possible that the viscosity enhancing agent, dispersion agent and all other components of the product including cementitious material, density modifiers, fibres etc may be dry mixed together and then made into a paste or slurry by addition of water.

30 Alternatively, some of the solid components eg cementitious material, lime, silica, density modifiers etc may be dry mixed with the viscosity enhancing agent thoroughly.

Water may then be added to pre-wet the mixture. The dispersion agent may then be dissolved in the rest of the water and added to the solution to the mix. Mixing is not required for any longer than five minutes. Total wet mixing time preferably should not exceed 15 minutes. The resultant mixture is then kneaded for say around five minutes depending upon the effectiveness of the kneading facility. In this regard long kneading times should be avoided.

The material can then be provided to the extrusion apparatus for use. Alternatively, a cementitious slurry or paste may be provided with the desired consistency, and suitable quantities of viscosity enhancing agent and dispersion agent may then be added as powder to the paste. In this instance, longer kneading time may be required to thoroughly mix the viscosity enhancing agent and dispersion agent in the paste.

If desired, the viscosity enhancing agent and dispersion agent may be provided to the cementitious slurry or paste via separate components of the FRC mixture. To explain, it may be appropriate to pre-treat the reinforcing pulp fibre with a dispersion agent. The cementitious material could be pre-dosed with a viscosity enhancing agent whereby it is combined with a dispersion agent upon mixing with the fibre.

It should also be understood that more than one viscosity enhancing agent and more than one dispersion agent may be used in the mixture.

The compositions formed in the above mentioned ways may be cured at ambient temperature and pressure or at higher temperatures and pressures. Curing methods such as steaming at high temperatures or autoclaving at high temperatures and pressures are possible. Unlike the prior art, the resultant extrudable cementitious material is suitable for autoclave curing. This is a further distinction over the prior art which use synthetic fibres unsuitable for autoclaving.

The exact regime of curing, such as pre-cure times, temperatures, pressures and cure times must be optimised for the specific formulation. As is well known, it is important for cementitious compositions to be prevented from drying out during curing to achieve optimum strength.

Compositions formed using the method of this invention show no adverse effects in terms of physical or mechanical properties during curing or afterwards when

compared to specimens made in the traditional way with high grade viscosity enhancing agents. In fact the use of dispersion agents appears to aid the forming of a superior surface finish.

5 The disclosed method and treatment agent are also particularly suitable for producing low density composite articles, that contain a high proportion of density modifying additives. Examples of such additives would be perlite, vermiculite, low density calcium silicate hydrate, ceramic hollow spheres, fly-ash etc. This invention can also be used with the addition of air entraining agents to modify density. Densities of 1.2 g/cm^3 or below may be achieved using the present invention.

10 In a further aspect, the present invention provides a method for forming a low density cementitious article comprising adding a cementitious material, density modifying additive, viscosity enhancing agent and dispersion agent to water, optionally with lime, silica, and fibre reinforcement, extruding the resultant paste and curing the extruded article wherein the density of the cured article is no greater than 1.2 g/cm^3 .

15 This invention also is suitable for compositions containing a variety of reinforcing fibres. Examples of such fibres would be wood pulp (cellulose) fibres, asbestos fibres, polymer fibres, glass or metal fibres. This is another advantage arising from the present invention. The prior art extrusion techniques are limited to particular fibres and particular fibre contents. The present invention allows an operator to choose the type
20 and quantity of fibre to specifically match the article to its desired use eg up to around 25% vol.

Further, it has been found that the addition of viscosity enhancing agent and dispersion agent provides an extruded product with an improved surface finish. It is not entirely clear why this occurs, however, the applicant has found clear visible
25 improvement in surface finish between extruded articles according to the present invention and those of the prior art. This is even true for articles with higher fibre contents ie 15% and above.

The present invention will now be described with reference to the following non-limiting examples:

EXAMPLE 1

A composition was prepared according to the materials and proportions indicated in Table 1, the solid components blended in a high speed Eirich mixer and then kneaded together with the water in a Hobart mixer. The paste produced was then extruded into sheets 50mm wide and 10mm thick using a Handle laboratory extruder with 75mm barrel. For each type of viscosity enhancing agent, repeat experiments were carried out with different addition levels to ascertain the minimum required for good extrusion, surface finish and shape retention. Table 2 lists the viscosity enhancing agents and dispersion agents trialed with some detail as to their origin, chemistry and cost. Table 3 lists the addition levels of viscosity enhancing agents and combinations of viscosity enhancing agents and dispersion agents that have equivalent performance in extrusion moulding and enables comparisons of the effect of the dispersion agent.

Table 1

Material	Details	Amount used
Fibre	Bleached softwood Kraft pulp from Weyerhaeuser. (size specs)	11% wt of solids
Cement	OPC Type 1 from Blue Circle Southern	Cement : Silica 60:40
Silica	200G milled quartz	Cement : Silica 60:40
Water		30% of total weight

Table 2

Type	Details	Cost
VEA1	Shin-Etsu 90SHV-WF Hydroxyethyl methyl cellulose (HEMC) (12,000 mPas, 1% solution @ 20° C, Brookfield)	US\$8.00/kg
VEA2	Wolff Walsrode Walocel VP-M20677 Hydroxyethyl methyl cellulose (HEMC) (75,000-85,000 mPas - 2% solution @ 20° C, Haake Rotovisko)	US\$7.41/kg
VEA3	Dow J75 Hydroxypropyl methyl cellulose (HPMC) (75,000 mPas, 2% sol. And 3000 mPas, 1% sol.@ 20°C, Ubbelohde tube)	US\$8.50/kg
VEA4	Union Carbide Cellosize QP 100MH Hydroxyethyl cellulose (HEC) (4000-6000 mPas, 1% solution @ 25° C, Brookfield)	US\$6.50/kg
VEA5	Dow J20 Hydroxypropyl methyl cellulose (HPMC) (20,000 mPas, 2% sol. And 900 mPas, 1% sol.@ 20°C, Ubbelohde tube)	
VEA6	Sigma Aldrich-41,933-8 Carboxy methyl cellulose (CMC) Av.Mol.Wt. 700,000 Degree of substitution = 0.9	
DA1	SKW Melment F15 Sulfonated melamine formaldehyde (SMF)	US\$2.80/kg

Table 3

	Amount required without DA1	Amount required with 0.2% DA1	Cost of formulation US\$/tonne	
			OLD	NEW
VEA1	1.5%	1.2%	158.22	145.38
VEA2	1.5%	1.2%	151.98	140.39
VEA3	1.75%	1.5%	163.89	149.92
VEA4	Inadequate performance	1.2%	-	132.77

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EXAMPLE 2

A composition was prepared according to the materials and proportions specified in Table 4. The solid components were blended in a high speed Eirich mixer and

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subsequently mixed with a water/VEA solution in a Hobart mixer. The paste produced was then extruded into sheets 50mm wide and 10mm thick using a Handle laboratory extruder with 75mm barrel. For each type of viscosity enhancing agent, repeat experiments were carried out with different addition levels to ascertain the minimum required for good extrusion, surface finish and shape retention. Table 6 shows the levels of viscosity enhancing agent required using the method of the new invention and without.

Table 4

Material	Details	Amount used
Fibre	Bleached softwood Kraft pulp from Weyerhaeuser. (size specs)	9% wt. of solids
Cement	OPC Type 1 from Blue Circle Southern	Cement : Silica 60:40
Silica	200G milled quartz	Cement : Silica 60:40
Density	Low density calcium silicate hydrate	10% wt of solids
Modifier		
Water		38% of total weight (41% when VEA6 is used).

Table 5

	Amount required without DA1	Amount required with 0.3% DA1	Cost of Formulation US\$/tonne	
			OLD	NEW
VEA3	2%	1.8%	183.11	177.68
VEA4	Inadequate performance	1.8%	-	154.84
VEA5	Inadequate performance	2%	-	-
VEA6	Inadequate performance	2.2%	-	147.63*

* Estimated price

EXAMPLE 3

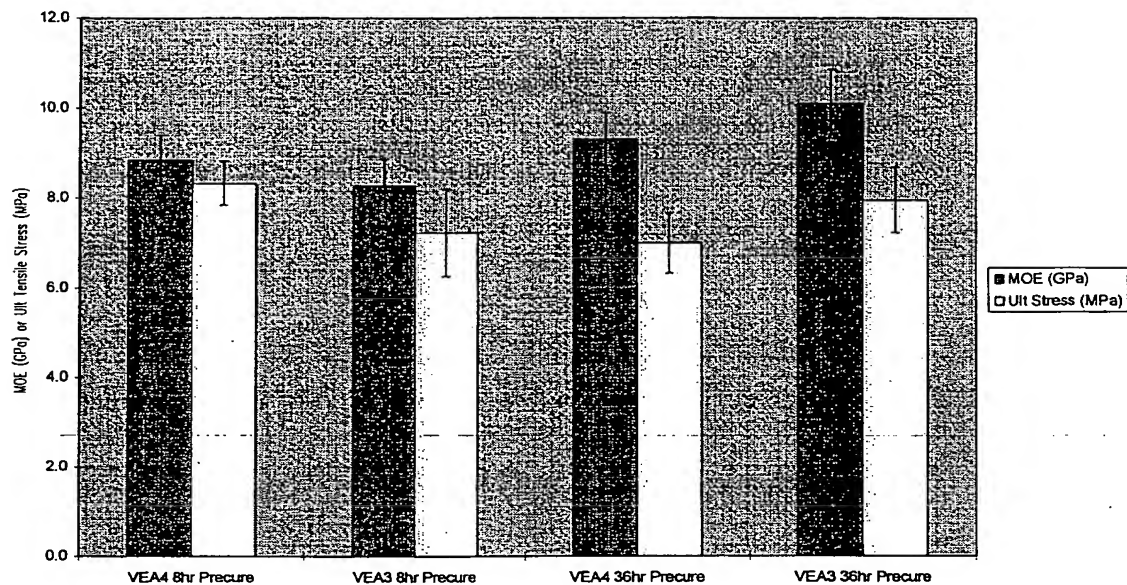
Two compositions, one containing VEA3 (Mix 1) and the other VEA4/DA1 (Mix 2) were prepared according to the materials and proportions specified in Table 6. VEA3 is a high grade HPMC and VEA4 is a cheaper HEC compound. For each, all the solid components were blended in a high speed Eirich mixer. The dry solids were then kneaded together with the water in a Hobart mixer till a homogenous paste was formed.

The paste produced was then extruded into sheets 50mm wide and 10mm thick using a Handle laboratory extruder with 75mm barrel. Half the samples were pre-cured at ambient conditions for 8 hours and the other half at ambient conditions for 36 hours. The strips were then cured in an autoclave under saturated steam pressure at 177° C for 8 hours. The mechanical properties of the two compositions were tested, and Graph 1 shows the results. It can be seen that there is no significant difference in the measured mechanical properties between samples made with VEA3 and VEA4/DA1. It was also observed that the sample made with VEA4/DA1 had the better surface finish of the two.

Table 6

Material	Details	Amount-used
Fibre	Bleached softwood Kraft pulp from Weyerhaeuser. (size specs)	9% wt. of solids
Cement	OPC Type 1 from Blue Circle Southern	Cement : Silica 60:40
Silica	200G milled quartz	Cement : Silica 60:40
Density	PQ Extendspheres (hollow ceramic spheres, effective density ~0.7 g/cc)	10% wt of solids
Water		30% of total weight
VEA3	As in Table 2	2% in Mix 1
VEA4	As in Table 2	2% in Mix 2
DA1	As in Table 2	0.3% in Mix 2

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Graph 1

Dated this 26th Day August 1999

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